

Pretreatment of Wool/Cotton for Union Dyeing

Part 2: Fiber Reactive Quaternary Ammonium Compounds

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The resurging interest in wool/cotton fabrics for interiors and apparel has led to recurrent investigations in improving dyeing and finishing.¹⁻¹¹ Textile manufacturers and consumers generally recognize wool/cotton textiles as superior products that combine the rich full hand of wool with the comfort of cotton. The diametric yet complementary properties of these fibers include wool's high elongation and weakness at low stress and cotton's resistance to elongation and strength at high stress. Wool's low thermal conductivity and hygroscopicity, leading to apparent dryness, complement cotton's propensity to dissipate heat and absorb moisture quickly for easy wettability. While cotton maintains high thermal conductivity, wool retains low thermal conductivity up to moisture regains of about 15%. Thus, wool/cotton fabrics are ideal for outdoor sports where exposure to spray

and rain is a possibility and they are unique for all-season textiles and apparel.

As the interest in wool/cotton fluctuates, the lack of sustained availability, and thus acceptance, has been tied to the actual sourcing of yarn, fabric, and apparel. Part of the sourcing problem is due to the difficulty in dyeing wool/cotton to union shades. This problem was addressed at the fundamental level by chemically modifying cotton to make it equally competitive with wool in the dyebath. An earlier report covered investigations of resin/ethanolamine (MEA) formulations.⁹ The resins were derivatives of glyoxal and urea including conventional *N,N*-dimethyloldihydroxyethyleneurea (DMDHEU) and two modified DMDHEU's—the *N,N*-dimethylated analog, DHDMI (no formaldehyde release resin, NFR), and the glycolated DMDHEU (low formaldehyde release resin, LFR)—with wool/cotton union

cloth in a padbath. The best results for union dyeing by C.I. Reactive Blue 69 (vinylsulfone type) were obtained with LFR/MEA at 1%, 2%, and 3% dyeings and with NFR/MEA at 0.3% and 1% dyeings. Physical tests showed optimum retention of mechanical properties and highest rated colorfastness to light, drycleaning, washing, wet and dry crocking, and staining. Part 1 of this report covered investigations of these same resins with choline chloride applied similarly to wool/cotton union fabric.¹² In this case, union shades were achieved from 1% to 3% dyeings with C.I. Acid Red 114. Physical testing showed acceptable retention of mechanical properties; excellent colorfastness to drycleaning, washfastness color change, and dry crocking; moderate fastness to wet crocking and light; and poor washfastness stain.

This study was expanded to include commercial dye fixatives with fiber reactivity to cellulose for adding qua-

ABSTRACT

Commercial dye fixatives, including those with fiber reactivity and amino, quaternary, and cationic nitrogen, were examined as pretreatment compounds for ionic dye attraction in dyeing wool/cotton to union shades. Some fixatives were ionically bound to wool and cotton and some were chemically bound through epoxide and azetidinium ring openings or through guanidino functions to impart amino and quaternary ammonium functionality. A monomeric fiber-reactive quaternary (FRQuat) fixative with quaternary ammonium and epoxide reactivity was examined as a prototype because of its simple structure and small molecular size.

KEY TERMS

Cotton
Dye Fixatives
Union Dyeing
Wool

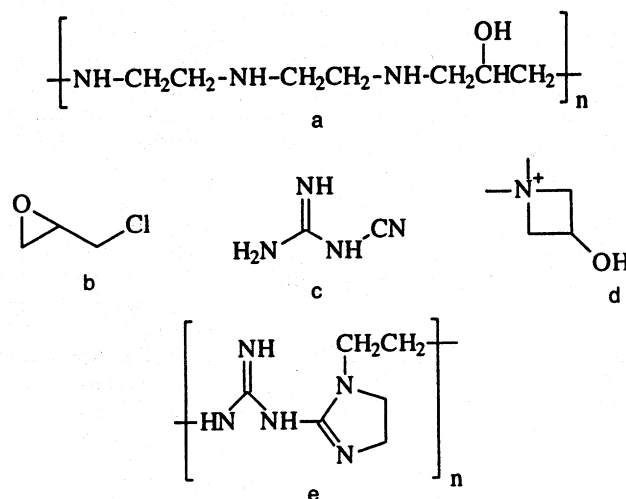


Fig.1. Formation of polyamino condensation products from the polymerization of alkyl di- or triamines.

- 2,2'-diaminodimethylamine, $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$, diethylenetriamine.
- Epichlorohydrin.
- N*-cyanoguanidine.
- Epoxy, azetidinium reactive sites.
- Guanidino reactive sites.

ternary nitrogen (FRQuats) and/or amino functionality to cotton cellulose. Some of the fixatives were merely ionically bound to cellulose and others reacted covalently through epoxide, azetidinium, or guanidino functions. All were applied in basic medium as pretreatment compounds before dyeing with Acid Red 114. FRQuats were of interest as alternatives to resin/amines because they were applied to the fabrics from wet baths. The investigations were aimed at finding comparable, successful procedures using wet pretreatments in place of pad-dry-cure processes for union dyeing wool/cotton blends.

Experimental

Several fiber reactive fixatives were supplied in aqueous form as either pretreatments or aftertreatments for fixing dyes to cellulosic textiles. All of the fixatives were polyamino condensation products (Fig. 1) formed from the polymerization of alkyl di- or triamines. The product in Fig. 1a is derived from 2,2'-diaminodiethylamine, $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$, diethylenetriamine, mostly with epichlorohydrin (Fig. 1b) but in one instance with *N*-cyano-guanidine (Fig. 1c). Some merely reacted ionically to form insoluble complexes with the textile's sorbed dye to resist color loss upon laundering. Many of these condensation products, however, offered reactive sites: epoxy, azetidinium (Fig. 1d) or guanidino (Fig. 1e) groups. These groups allowed reactions with cellulose anions of cotton, lysinyl amino groups, or broken disulfide linkages in wool. Such reactions led to covalent attachment of the condensation products to the fibers. All of these fixatives imparted a rich reservoir of amino groups to the fibers for dye attraction under acidic conditions.

Although most of these compounds were designed for application as post-treatments to dyeing, they were applied from basic solutions at room temperature prior to dyeing.

Pretreatment Conditions

Extensive investigations using Quat 188 (Dow Chemical Co.,^a Midland,

^a Mention of a brand or firm does not constitute endorsement by the U.S. Department of Agriculture or the American Association of Textile Chemists and Colorists over other brands or firm names not mentioned.

Mich.; 3-chloro-2-hydroxypropyltrimethylammonium chloride, Fig. 2) as a simple monomeric FRQuat prototype were carried out to determine the optimum reaction conditions for forming epoxide without degrading wool by excessive shrinkage, embrittlement, unacceptable fabric handle, or fabric strength loss.

¹³C NMR Spectroscopy

To provide evidence for the epoxide formation of the prototype Quat 188 and its reaction with anionic cotton cellulose, its chemical modification by nuclear magnetic resonance (NMR) spectroscopy was followed. The epoxide reaction of Quat 188 is well documented.¹³ Quat 188 was applied under the alkalinity conditions that are undamaging to wool in the wool/cotton fabric blend—pH 11, three hours, and room temperature. Since these conditions were mild for epoxide formation, ¹³C NMR was used to provide evidence for its formation and reactivity with cotton cellulose. All ¹³C NMR spectra were obtained using Waltz decoupling on a Varian Gemini-200 spectrometer operating at 50.3 Mhz. Typically a 45°C degree pulse width was used with a one-second recycle time. Spectra of the Quat 188 were obtained from samples prepared by the addition of 0.5 mL of the reagent to 0.5 mL of D₂O. Chemical conversions to epoxide and cellulose ether were performed in D₂O at 20°C using NaOD to adjust the pH to 11. The progression from unreacted chlorohydrin to reactive epoxide could be observed.

Fixative Uptake

The FRQuat polymeric fixatives were used to pretreat wool/cotton fabrics at pH 11, three hours, and room temperature. After pretreatment and before dyeing, cotton yarns were removed from the union cloth to determine the nitrogen content and actual add-on of reagent, which are shown in Table II.

Pyrolysis GC

To provide further evidence for reactivity, pyrolysis gas chromatography (Py-GC) analysis was carried out on 200-microgram samples of pretreated cotton and wool yarns. The conditions for collecting pyrograms were the same as those reported in a previous Py-GC study of Hercosett resin on wool.^{9,14}

Materials and Methods

A pre-study involved Quat 188 (65% solids; Dow Chemical), a simple monomeric chlorohydrin quaternary ammonium compound and model fixative. All fabrics were from Testfabrics in Middlesex, N.J. Four fabrics were pretreated: TF400M (mercerized cotton), TF400U (unbleached, desized cotton print cloth), TF530 (wool challis), and TF4504 (62% wool/38% cotton union fabric, 48 x 44 fabric count, wool warp and cotton filling). The FRQuat dye fixative study involved three fabrics: mercerized cotton print cloth TF400M, all-wool TF530, and wool/cotton TF4504. They were pretreated with commercial dye fixatives Solfix E, Sandospace HPB Liquid, Sandene 8425, Levogen FSE, and Freetex 670 Fixative and R10110-87 Fixative. These compounds were supplied as aqueous solutions containing approximately 30-50% solids. A typical pretreatment bath was formulated as follows:

- The bath was constituted at a 30:1 liquor ratio for a 10-gram fabric sample (300 mL bath volume) where the fixative was added as 20% on the weight of the bath (owb); i.e., 60 mL.
- The pretreatment bath was formulated to pH 11 with sodium hydroxide.
- The fabrics remained in the bath solution for three hours at room temperature.

The fixatives are described as follows: Epoxyquaternary ammonium compounds

- Solfix E (Ciba Corp., Greensboro, N.C.): polyamino chlorohydrin quaternary ammonium polymer with epoxide reactivity.
- Sandospace HPB Liquid (Clariant Corp., Charlotte, N.C.): amino chlorohydrin quaternary ammonium salt with epoxide reactivity.

Azetidinium quaternary ammonium

- Levogen FSE (Bayer Corp., Rock Hill, S.C.): polyamino cationic ammonium polymer with azetidinium reactivity.

Cyanoguanidine polyamine

- Sandene 8425 (Clariant Corp., Charlotte): polyamino cationic polyamino cyanoguanidine sulfate formulation.

Others

- Freetex 670 Fixative (Freedom Textile Chemicals Co., Charlotte): polyamino quaternary ammonium polymer.
- R10110-87 Fixative (Freedom Textile Chemicals Co.): experimental: lower molecular weight Freetex 670 variety.

These pretreatments were followed by dyeing from a fresh bath. The dye,

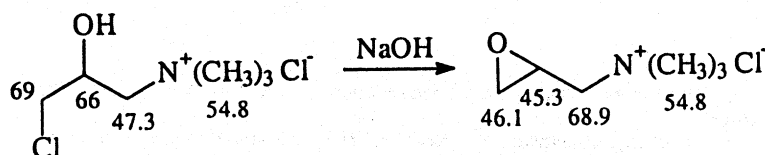


Fig. 2. Formation of 2,3-epoxypropyl-trimethylammonium chloride from 3-chloro-2-hydroxypropyl-trimethylammonium chloride under alkaline conditions.

Acid Red 114, was processed according to the conventional protocol of pH 4.5-5.5, liquor ratio 20:1, 10% Glauber's salt, 1C/min temperature rise to 90C, and dyeing at that temperature for 60 minutes. Light, medium, and heavy union shades were produced at dyeings of 1%, 2%, and 3%, respectively.

Results and Discussion

¹³C NMR Spectroscopy Evidence for the Reactivities of FRQuats

Product information for Quat 188 indicates that the compound is supplied as aqueous chlorohydrin, which under alkaline conditions forms the epoxide in Fig. 2.¹³ the figure shows the ¹³C NMR shift values assigned in ppm.

The epoxide is reactive from 20C-50C, 0-400 hours, and at pH 10.5-12.5. At pH 12.5 and 20C, *t*_{1/2} is 45 hours. At pH 11.0 and 20C, *t*_{1/2} surpasses 400 hours.¹³ At pH 14, however, the epoxide is hydrolyzed to the unreactive diol shown in Fig. 3 by 21 hours.

The salient reaction is soda cellulose combining with the epoxide (Fig. 2) in basic medium to form etherified cellulose according to Fig. 4.

Under these reaction conditions, ¹³C NMR spectroscopy validated the reactive epoxide species and the reaction to form cellulose ether.

Table I shows that it is not possible to achieve union shades in three hours at pH 11 and 20C. It was observed that Acid Red 114 was selectively taken up by the wool yarns and the cotton yarns were only stained. Thus, the optimum conditions for cotton dyeing were not appropriate for wool/cotton for union shades.

Nitrogen Analysis for Fixative Uptake

Table II shows the results of Kjeldahl nitrogen analysis of the fixatives and cotton components of the pretreated fabrics. The results from cotton indi-

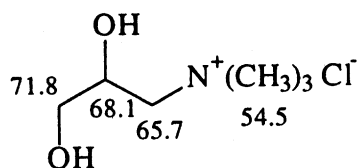


Fig. 3. Unreactive diol from 2,3-epoxypropyl-trimethylammonium chloride.

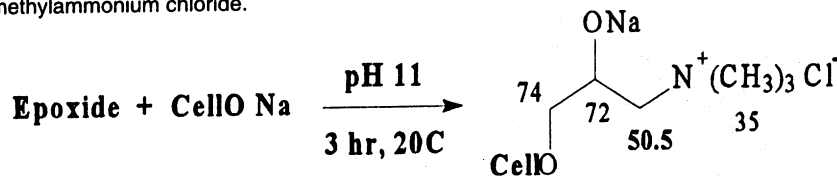


Fig. 4. Formation of etherified cellulose from 2,3-epoxypropyl-trimethylammonium chloride and soda cellulose.

Table I. Effects of Reacting Quat 188 with Cotton, Wool, and Wool/Cotton Fabrics under Various Conditions of Pretreatment

Conditions, Fabric Sample	Quat 188 (% owb)	K/S	% Dyeing, Observations
pH 13.5, 5 hrs, 20C			
cotton, mercerized	20	13.1	1%, skittery shades
cotton print cloth	20	12.0	1%
wool	20	30.9	1%, excessive shrinkage in wool
pH 12, 3 hrs, 20C			
cotton print cloth	20	4.27	1%
wool/cotton union fabric	20		no union shade
pH 12, 4 hrs, 40C			
cotton, mercerized	10	25.6	3%, optimum
cotton print cloth	10	11.4	3%
wool	10	38.9	3%, damaged
wool/cotton union fabric	10		no union shade
pH 11, 3 hrs, 20C			
cotton print cloth	20	3.62	1%, optimum for wool/cotton
wool	20	31.4	1%, no damage to wool
wool/cotton union fabric	20		1%, no union shade

Table II. Percent Nitrogen Content of Fixative Compounds and % Add-On for Cotton Yarns

Pretreatment Fixatives	Fixative (Dry State) %N	Pretreated Cotton		Pretreated Wool/Cotton Fabric (cotton yarns)	
		%N	%Add-On	%N	%Add-On
Quat188	9.20	0.22	2.40	0.13	1.41
Solfix E	5.19	0.16	3.04	0.16	3.08
Sandospace HPB	4.02	0.10	2.49	0.14	3.48
Sandene 8425	31.6	0.60	1.90	0.66	2.09
Levogen FSE	9.34	0.14	1.47	0.13	1.40
Freetex 670	9.50	0.13	1.38	0.10	1.03
R10110-87	9.12	0.11	1.21	0.21	2.30

cate the extent of chemical modification. Note also the high nitrogen content of Sandene 8425 and the Sandene 8425-treated cotton.

Pyrolysis GC Evidence for the Reactivities of FRQuats

The following observations were made by pyrolysis-GC to further substantiate reactivity:

- Comparisons of pyrograms showed that wool and cotton are unaffected by the pretreatment conditions of pH 11, three hours, and 20C when no fixative is present in the pretreatment bath.
- Pyrograms of wool and cotton treated with Quat 188 for three hours at pH 11 and 20C showed a peak enhancement at 16 minutes for wool but no distinct peak for cotton.
- An enhanced peak at 16.5 minutes in the wool/Solfix E pyrogram was common to Solfix E and not present in wool alone.

- Pyrograms showed new peaks for cotton/Solfix E at 26, 28, and 33 minutes that were common to Solfix E.
- Pyrograms of wool pretreated with Freetex 670 Fixative and R10110-87 showed a strongly enhanced peak for wool/Freetex 670 Fixative and R10110-87 that was common to the fixative alone at 16.5 minutes. This was a minor peak present in the pyrogram of untreated wool.
- Cotton pretreated with Freetex 670 Fixative and R10110-87 showed no new peaks that could be attributed to the reaction of cotton with the fixative.
- Pyrograms of wool pretreated with all fixatives, including Quat 188, show a strongly enhanced peak at 16.5 minutes.
- The pyrograms of cotton pretreated with Solfix E, Levogen FSE, Sandene 8425, and Sandospace HPB Liquid, all show new peaks at 25.7, 28.3, and 32.5 minutes. which are absent in the pyrogram of untreated cotton.

Color Strength and Union Shades

Table III compares the effects of FRQuat pretreatments for K/S values and Union Shade Index, *F*, on dyeing with Acid Red 114. *F* values are derived from digital image analysis which provides objective measurement

Table III. Effects of FRQuat Fixatives on Coloration and Union Shade of Cotton, Wool, and Wool/Cotton Blended Fabrics

Pretreatment Fixatives	K/S ^a			Union Shade Index, F ^b		
	1%	2%	3%	1%	2%	3%
Cotton M						
none	2.65	2.34	3.99			
Solfix E	7.45	13.9	15.2			
Sandospace HPB	^d	^d	^d			
Sandene 8425	6.75	13.6	17.9			
Levogen FSE	4.79	12.8	14.7			
Freetex 670	5.53	14.1	15.4			
Wool						
none	20.0	26.3	27.7	11.8 ^c	8.30 ^c	7.22 ^c
Solfix E	14.0	22.5	24.6			
Sandospace HPB	^d	^d	^d			
Sandene 8425	14.0	21.7	23.4			
Levogen FSE	7.93	13.7	18.9			
Freetex 670	8.50	14.9	19.9			
Wool/Cotton Union						
none	3.39	3.63	4.40	66.9	47.3	41.9
Solfix E	12.5	20.1	22.3	14.5	10.5	10.5
Sandospace HPB	13.0 ^d	18.2 ^d	20.7 ^d	15.1	12.1	3.79
Sandene 8425	9.47	20.6	24.4	15.3	9.74	9.74
Levogen FSE	8.35	12.6	15.6	15.5	13.0	11.5
Freetex 670	7.45	12.2	15.0	16.5	12.2	4.97
R10110-87	8.02	13.5	15.4	14.7	7.97	10.6

^a The Color Machine (BYK-Gardner) was used to obtain Kubelka-Munk equation K/S values, which are directly related to color intensity. ^b Digital images were displayed as (pixel intensity vs. gray level) histograms for measurement of union shade (F). For bimodal histograms, $F = (M_{\text{high}} - M_{\text{low}})(P_{\text{small}}/P_{\text{total}})$, where F = union shade index; M_{high} and M_{low} = gray scale values for highest and lowest peaks, respectively; P_{small} and P_{total} = respective peak areas. ^c For trimodal histograms, $F = (M_{\text{right}} - M_{\text{center}})(P_{\text{right}}/P_{\text{total}}) + (M_{\text{center}} - M_{\text{left}})(P_{\text{left}}/P_{\text{total}})$, where M and P values represent gray scale and peak areas of each of three peaks. Thus, in trimodal histograms the F value is the sum of F values for the center-left pair and the center-right pair of peaks. Low F values represent union shade. ^d Data usable as control values alternative to gray card value. ^e High K/S but hue shift from red to orange.

of a union shade from the histograms of digitized fabric images.¹⁵

The cationic fixatives dramatically increase dye uptake on cotton and slightly inhibit dye uptake on wool. K/S values for wool and wool/cotton fabrics show that at 2% and 3% dyeing, Solfix E and Sandene 8425 give the highest color depths. For pretreated cotton, Freetex 670 is equally effective. Although Sandospace HPB-pretreated union fabrics are also high in K/S, the hue shift from orange-to-red (see point d in Table III) mitigates its importance.

Microscopy

Evidence for dye penetration and ring dyeing was obtained from wool and cotton fiber cross sections. Sample fibers were assembled with undyed wool fibers as a support. The fiber collection was placed in a Micro Schwartz-type fiber microtome (no. 200-A, Micro Instruments, Marshfield Hills, Mass.). The fixation compound was Collodian (Mallinckrodt U.S.P.). Sections were cut to 15- to 20-micron thicknesses and viewed at 400x to 500x on an Olympus BX-50 microscope.

Physical Property Measurements

Table IV indicates the dimensional stability of pretreated all-cotton (TF400U), all-wool (TF523), and wool/cotton union cloth (TF4504). The improvement in overall dimensional stability for wool in wool/cotton was at

least 50%. Table V shows fabric strengths and extensions.

Table IV. Percent Shrinkage of Pretreated, Undyed Cotton, Wool, and Wool/Cotton Fabrics

Pretreatment Fixatives	% Shrinkage ^a				
	Cotton M Overall Area	Wool Overall Area	Wool/Cotton Fabric		
			Warp (wool)	Weft (cotton)	Overall Area
Solfix E	8.32	12.7	3.42	8.25	11.4
Sandospace HPB	7.76	10.6	2.17	8.75	10.7
Sandene 8425	7.92	14.6	4.25	9.33	13.2
Levogen	7.20	14.3	3.42	8.67	11.8
Freetex 670	6.97	13.6	3.83	8.75	12.2
R10110-87	7.13	14.1	3.92	8.75	12.3
Control (no pretreatment) ^b	10.2	10.9	3.70	2.70	6.3

^a After five machine wash/tumble dry cycles according to AATCC Test Method 135-1992. ^b Treated as blanks; subjected to all conditions except pretreatment formulations.

Table V. Retention of Breaking Strength and Extension after Pretreatments with Dye Fixatives.

Pretreatment Fixative	Cotton M	Wool	Wool/Cotton Union Fabric ^a
%Strength Retained			
Solfix E	94.2	92.5	94.1
Sandospace HPB	93.8	99.9	104.0
Sandene 8425	98.2	95.8	96.4
Levogen FSE	97.1	96.7	94.2
Freetex 670	97.6	99.0	97.8
R10110-87	95.0	92.4	97.8
%Extension Retained			
Solfix E	113	97.3	92.8
Sandospace HPB	119	107	100
Sandene 8425	118	104	102
Levogen FSE	122	104	99.3
Freetex 670	111	98.6	95.5
R10110-87	115	107	100

^a Wool warp direction.

Fastness Properties

The wool/cotton fabrics pretreated FRQuat and other dye fixatives were subjected to fastness tests according to the standard test methods: AATCC Test Method 61, Colorfastness to Laundering, Home and Commercial; Accelerated (Conditions IIA); AATCC Test Method 8, Colorfastness to Crocking, Crockmeter Method (wet and dry conditions); AATCC Test Method 132, Colorfastness to Drycleaning; and AATCC Test Method 16E, Colorfastness to Light (20- and 40-hour increments.) Table VI shows these results.

Discussion

The objective of this work was to chemically modify cotton by introducing protonated amino groups or quaternary ammonium groups so the cotton in wool/cotton fabrics would dye competitively with wool. The perennial problem in dyeing union shades has been selective dye uptake by wool—cotton emerges only stained and the end product is chambray. The availability of wool/cotton textiles would increase if the problems of union dyeing could be solved and the concept and ease of dyeing union fabric were introduced into new piecegoods and apparel markets. It was successfully demonstrated that the pad-

Table VI. Fastness Properties of Pretreated Wool/Cotton Fabrics Dyed with C.I. Acid Red 114.

Pretreatment Fixatives	Croaking		Drycleaning	Washfastness Color Change	Washfastness Staining ^a	Lightfastness	
	Wet	Dry				20 hrs.	40 hrs.
1% Dyeing							
Solfix E	2	3	5	5	1	2	1
Sandospace HPB	1-2	3	5	3	1	4-5	3-4
Sandene 8425	2	3	5	4	1	2-3	1-2
Levogen FSE	1-2	2-3	5	3-4	1	2-3	1-2
Freetex 670	1	3	5	4-5	3-4, 2 3, 3-4, 4-5, 4	3	2
Freetex 670, then extraction after dyeing ^b	1	3	5	4-5	3, 2, 3-4, 3-4, 4, 4	3	2
Freetex 670, then fixative after dyeing ^c	1	2-3	5	4-5	3, 1-2 3, 3	3	2
Freetex 670, then extraction and fixative after dyeing ^d	1	3	5	4-5	4-5, 4 3, 1-2, 3, 3-4, 4-5, 3-4	3	2
R10110-87	2	2-3	5	2-3	1	3	1-2
2% Dyeing							
Solfix E	2	3	5	5	1	2	1
Sandospace HPB	1	2-3	5	3	1	4-5	3-4
Sandene 8425	1	2-3	5	3-4	1	2-3	1-2
Levogen FSE	1	2-3	5	3-4	1	3-4	1-2
R10110-87	1	2	5	3	1	3-4	2
3% Dyeing							
Solfix E	1	2-3	5	5	1	2	1
Sandospace HPB	1	3	5	3	1	4-5	3-4
Sandene 8425	1	2-3	5	4	1	2-3	1
Levogen FSE	1	2	5	3	1	3	1-2
Freetex 670	1	2	5	4-5	1	2-3	1-2
R10110-87	1	2	5	2-3	1	3-4	2

^a Washfastness stain ratings are given for the individual fiber types: acetate, cotton, nylon, polyester, acrylic, and wool, respectively. Single ratings indicate cotton staining where no other fiber staining was evident. ^b Soxhlet extraction with dimethylformamide/water, 50/50 after dyeing. ^c Aftertreatment with Freetex 670 Fixative after dyeing. ^d Extraction followed by aftertreatment with Freetex 670 Fixative after dyeing.

dry-cure applications of DMDHEU-G/MEA and DHDMI/MEA are successful pretreatments for union dyeing wool/cotton fabrics with Reactive Blue 69.⁹ Epoxy, azetidinium, and guanidino compounds were observed for the ability to apply them to the fabric from their solutions and for their high reactivities with anionic cellulose to form positively charged cotton. Dye fixatives capable of cationizing cotton by bonding to anionic cellulose through ionic forces of attraction were also examined. All the fixatives enrich wool and cotton in amino functionality, which in turn raises the affinity of those fibers for dyes. Acidic dyeing with Acid Red 114, a milling acid wool dye, was chosen to effect ionic attraction of the dye for the newly formed cationic cotton.

NMR spectra showed that at pretreatment conditions minimizing wool damage (pH 11, three hours, 20°C), Quat 188 formed an epoxide that reacted to form the modified, cationic cellulose alkyl ether. These reaction conditions were viable for parallel studies with polymeric FRQuats. Although union shades with QUAT 188 (Table I) were not obtained, union shades under these conditions were acquired with the polymeric fixatives (Table III).

All of the polymeric FRQuats produced appreciable nitrogen uptake by

cotton (Table II). After pretreatments with these compounds, *K/S* values were dramatically increased for cotton and wool/cotton at all dye concentrations (Table III). In the case of wool, dye uptake was inhibited at 1% but only slightly retarded at 2% and 3%. Union shades were produced in all of the pretreated wool/cotton fabrics. Solfix E, Sandospace HPB, and Sandene 8425 gave the highest *K/S* values (Table III).

The effect on dimensional stability of these fixatives (Table IV) shows that cotton is minimally improved, all-wool is not. Shrinkage in the wool/cotton union fabric can be attributed to the wool. The overall shrinkage of 6.3% for wool/cotton fabrics justifies the "dryclean only" care label.

All pretreatments on cotton, wool, and wool/cotton union fabrics retained at least 90% strength. This is a vast improvement over the pretreatments using the conventional durable press resins.¹² The effects of the dye fixatives on fabric elongation are negligible, implying no change in the resiliency that wool brings to a wool/cotton blend.

Microscopic examination of fibers pretreated with Sandene 8425 Liquid and then dyed with Acid Red 114 showed evidence of ring dyeing in cotton, but uniform dye penetration in

wool. Evidently, the dye is associated with the fixative, which because of its polymeric nature diffused little from the cotton fiber surfaces. Ring dyeing would not preclude using dye fixatives for union shade provided the dye is colorfast. However, washfastness staining was poor and this was complicated by some loss of dye from wool to cotton. Two procedures were attempted to improve fastness: DMF/water (50/50) extraction to remove occluded dye and, in the case of Freetex 670, aftertreatment (to dyeing) with this same fixative. No improvement in colorfastness was found (Table VI). Colorfastness to drycleaning was excellent, moderate-to-good for washfastness color change, moderate-to-poor for dry crocking, but poor to wet/dry crocking and lightfastness (40-hour exposure) (Table VI).

Conclusion

In Part 1, DMDHEU-type resin/choline chloride systems were examined.¹² Previously, resin/ethanolamine systems were found to be highly effective in promoting union dyeing of wool/cotton-blended fabrics.⁹ In this study, an alternative process to pad-dry-cure was examined—that of solution application at room temperature. This alternative system used commercial dye fixatives formed from condensation

polymerization with bifunctional alkylamines and having fiber reactive groups along with cationic charge or amino functions. These compounds were successful in union dyeing wool/cotton, whereas the monomeric epoxy-counterpart was not. Polyamino dye fixatives that were capable of forming cationic cotton but were less reactive and noncovalent-bonding were also investigated. These also produced union shades in wool/cotton fabrics. It was concluded that the availability of added amino groups in all of these polymeric fixative compounds is essential for union dyeing wool/cotton with Acid Red 114. Obstacles for implementation are poor lightfastness, wet crocking, and washfastness staining. All fixatives examined in this study, whether covalently or ionically bonded to wool and cotton, exhibited the same washfastness limitations with Acid Red 114. Requiring the "dryclean only" label is justified.

By achieving union shades comparable in shade and depth to all-wool fabrics, the potential for using the compounds for union dyeing wool/cotton blends with the processing ease of dye-

ing wool alone was shown. To advance the wool/cotton concept, aftertreatments for FRQuat pretreatment systems to fix the dye or new fiber-reactive compounds capable of sorption and with high fixation leading to improved dye fastness need to be designed. The cooperation of manufacturers of dye and textile auxiliary compounds to design, manufacture, and supply other products with the pertinent chemistry for ease of dyeing wool/cotton to union shades will be necessary.

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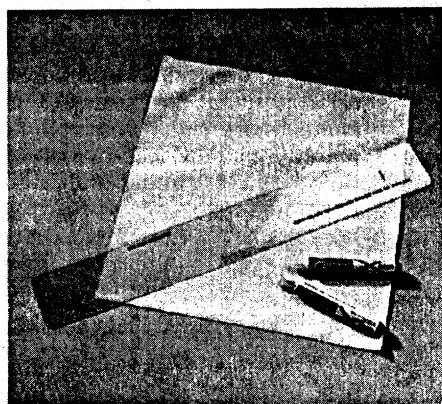
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